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Iontronics of Conjugated Polymers

－by looking back on the history of Iontronics－

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Iontronics deals with the phenomena and devices that involve the flow of both electrons and ions. This article is a good place to take a big picture look at where the field has been and where it is going. Iontronics could be dated back to as early as the discovery of electricity in the 18th century. This article devoted exclusively to the iontronics in organic electronic materials, therefore seems timely. I will provide merely my personal view on what occurred in the past that shaped the field as it is today. The field is intertwined with so many other fields that a complete review of its history and all the important discoveries is almost impossible. Therefore, in the convenience of space, I introduce the morphological control of polypyrrole (PPy) based on electrolysis technique.

1. Introduction

Conjugated polymers, both as semiconductors at the intrinsic state and as metallic conductors when heavily doped, have attracted broad interests since the discovery of conducting polyacetylene by Shirakawa, MacDiarmid Heeger, *et al.* in 1977. The possible application fields of conjugated polymers and semiconjugated polymers include electrode materials of batteries, electrochromism, modified electrodes, enzyme electrode, solid capacitors, polymer light emitting diodes, and polymer solar cells, *etc.* Most of applications are related to the electrochemical properties of the conjugated polymers. Meanwhile, electrolysis polymerization is the main preparation method for a number of widely used conjugated polymer films such as polypyrrole and polythiophene. Therefore, electrolysis polymerization and electrolysis properties of conductive polymers have been among the main research subjects of conjugated polymers since the early 1980s. This article reviews the scientific understanding and important scientific discoveries made on the electrolysis of conjugated polymers. In other words, by looking back on the history of **Iontronis**, I hope this article can further the field, and provide a reference for and insights into **Iontronic** organic electronic materials.

Iontronics deals with the phenomena and devices that involve the flow of both electron and ions. This article, devoted exclusively to the **Iontronics** in organic electronic materials, therefore seems timely.

2. Learn of the ion

We often hear a word “ion”. Then, what kind of things is the ion? On earth who would begin to use the word ion first? From now approximately 200 years ago, a researcher named Faraday, whom came to be called a father of the electromagnetism later, was in the U.K. Faraday thought when the electricity flowed to the material, the material is divided into two and one is attracted to the positive electrode which the electricity flows and another one to the negative electrode which the electricity flows. To this divided material, Faraday named "ion".

3. Electrochemical preparation of conjugated polymers

Among various synthetic methods of conjugated polymers, the electrolysis polymerization played an important role in the preparation of conductive polypyrrole, polyaniline, and polythiophene because the electrochemical approach has the advantage of one-step deposition of conjugated polymer films onto a metal electrode surface.

In general, electrolysis polymerization technique is performed with the electrolysis polymerization equipment shown in FIGURE 1. If the aromatization compound monomer that is to be polymerized is dissolved into a solvent containing a suitable supporting electrolyte and an appropriate voltage is applied to the electrode pair immersed into this solution, the monomer is ozidized or reduced on the surface of the anode or cathode, respectively, and it polymerizes in the form of a powder or a film and at times may show arborization. The case in which the monomer is oxidized and polymerized on the anode surface is called electrolysis oxidation polymerization. On the other hand, the case in which the monomer is reduced and polymerized on the surface of the cathode is called electrolysis reduction polymerization. The reference electrode might be immersed in the solution if necessary.

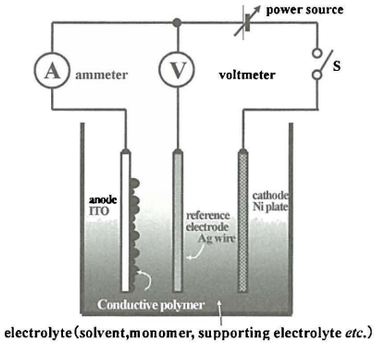
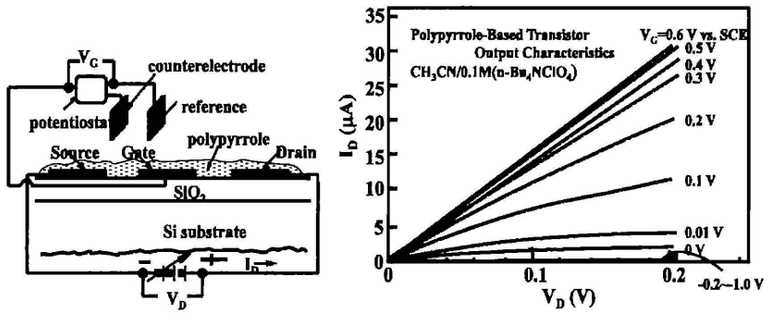


FIGURE 1. Electrolysis polymerization cell.

4. Iontronics

4.1 Electrochemical transistors using conductive polymers



H.S.White, G.P.Kittlesen, and M.S.Wrighton,
"Chemical derivatization of an array of three gold microelectrodes with polypyrrole: Fabrication of a molecular-based transistor",
Journal of American Chemical Society, **106** (1984) p.5375-5377.

FIGURE 2. Cross-sectional view of the device fabricated and representation of the circuit elements used to characterize it. Output characteristics of the transistor in CH_3CN/0.1 M $[n\text{-}Bu_4N]ClO_4$.

The electrical conductivity of these materials strongly depends on a doping level (oxidation level of the polymer main chain) for one of the most important characteristics of conductive pomer such as polypyrrole, polythiophene, polyaniline *etc*. Therefore an electric current flowing through the conductive polymer materials may be modulated, when an electrochemical signal to change this doping level is inputed. In addition, the change of this doping level should reply for the chemical input. Because not only it depends on electric potential to be set electrochemically, but also is caused by the redox-related materials. The first Organic Electrochemical Transistors was reported by Wrighton *et al.*[1] and utilized a potentiostat to control the conductivity of a polypyrrole layer, as shown in FIGURE 2.

4.2 Light-Emitting Electrochemical Cell

The first light-emitting electrochemical cell devices utilized a solution comprising one (or more) electrochemically active and luminescent organic compounds and an inert electrolyte as the liquid active material in a two (or three) electrode setup to create light in a process commonly termed solution electrogenerated chemiluminescence. The emitting mechanism of light-emitting electrochemical cell is as follows. An ion and cation radicals of emitting molecules are produced at each electrode by injected electrons and holes. These anion and cation radicals move due to ion conduction in the solution. Excitons of emitting molecules are produced by the collisions of both ion radicals. Emitting molecules emit fluorescence under the deactivation of the excitons.[2]-[4]

4.3 Conjugated polymers as actuators

Conjugated polymers with π electron conjugated system such as polyacetylene, polypyrrole, polythiophene and their analogies take three stages such as neutral, oxidized and reduced stages. The oxidized and reduced states are both highly conductive but the neutral state. The neutral conjugated polymer is electrochemically oxidized by ejecting electrons accompanied with doping of anions, viz. p-type doping or is electrochemically reduced by injecting electron with doping of cations, viz. n-type doping. The oxidized and reduced conducting polymer can be electrochemically reduced and oxidized to the neutral state releasing the dopants, respectively. Namely, either electrolysis oxidation or reduction cooperates with the doping of ions. For example, the redox, hence also called p-type dopin/undoping, can be written as following reaction,

$$CP^0 + A \underset{\text{undoping, } +e^-}{\overset{\text{doping, } -e^-}{\rightleftharpoons}} CP^+A^-$$

where CP represents a conducting polymer. CP^0 the neutral state which is insulative, and CP^+ the p-type doping state which is conductive. A^- is the dopant of CP^+. Therefore, the conjugated polymers swell and shrink upon doping and undoping, respectively. The conformation change of conjugated polymer during doping and subsequent volume change occurs.[5]-[7]

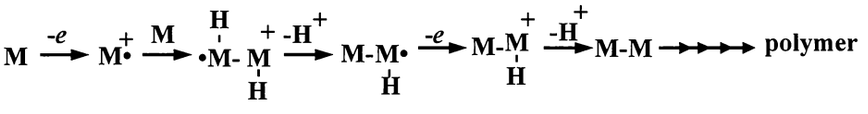
4.4 Biocompatibility of conjugated polymers

At present though it is made with a metal electrode such as ITO (indium tin oxide) and platinum as a nerve stimulation electrode, the compatibility of the bilological tissue and the metal electrode becomes a problem. As measures, up to date the surface of the electrode was covered by having used collagen that was one of the matrie cell (rxisting supermolecular structure besides the cell inorganism) and poly(lysine) that

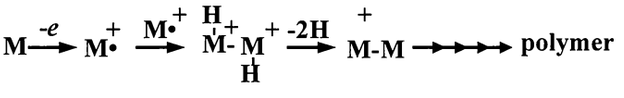
was the cell attachment factor (intercellular bonding) and compatibility was given. However, it caused an increase in impedance by covering the surface of the electrode and decreased the efficiency of the input and output stimulus signals. Therefore, the development of the nerve stimulation electrode in which compatibility with the biological tissue is possessed, and the efficiency of the stimulus signal is not decreased is necessary, and it is extremely important in progressing the nerve interface technology. If such conductive polymers have a high biocompatibility compared with the metal, the functional application in biomedical engineering as a new artificial internal organ material is expected. For example, fibroblast L929 cell of the mouse uniting organization origin was sown to the conjugated polymer film, polypyrrole, PPy and/or poly(3,4-ethylenedioxytthiophene), PEDOT, and the proliferative process of these cells was observed. The L929 fibroblastic cell was observed to proliferate almost similarly with the cell cultured without changing the form on a dish on the market and to maintain compatibility. That is, it has been understood that of the two kinds of conjugated polymers used by the actual experiment, the PEDOT films maintain the secretion function of the cell cultured on the surface. Therefore, the PPy- and the PEDOT-coated electrode suggested the possibility of being used as a nerve stimulation electrode with biocompatibility because it was effective to culture the cell.[8]

4.5 Technology for organic molecular communication

To date, various conductive polymers have been synthesized, but polypyrrole (PPy), whose molecular structure is shown in  , is the most stable after doping and is one of the most attractive materials, together with polyaniline, PAN, and poly(3,4-ethylenedioxythiophene), PEDOT, because of their good environmental stability and relatively high electrical conductivity. The polymerization reaction is thought to be either reaction 1, the electrophilic substitution coupling reaction, or reaction2, the radiacal coupling reaction, here M indicates a monomer, as shown in FIGURE 3.



Reaction 1 : electrophilic substitution coupling reaction



Reaction 2 : radical coupling reaction

M : monomer

FIGURE 3. Prospective electrolysis polymerization reaction mechanism.

In 1987 Kaufman *et al.* had reported fractal phenomena based on electrolysis polymerizaion reaction for the first time[9]. And also, similar phenomena have been found by Yoshino *et al*[10]. However, the polymerization reaction mechanism itself becomes very complex and a united opinion is not obtained. Though fractal growth phenomena in the electrolysis polymerization are seen in various places of the natural world, we are investigating the fractal growth phenomena and the form of polymers putting molecular communication and molecular machine on the mind.

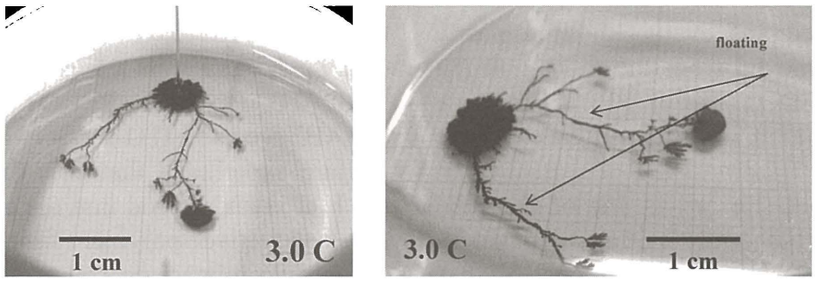


FIGURE 4. Control of PPy growth morphology based on applied current. Py : 5 mol/*l* , acetonitrile / 0.01 mol/*l* (n-Bu)$_4$*p*-TS, volume : 10 *l* , The applied current has been changed with 1 mA by 0.5C, 3 mA by 2.5 C and 5 mA by 3.0 C. The growth pattern changed two dimensional broad leaf (3 mA) to three dimensional needle leaf (1 mA) and to two dimensional broad leaf (5 mA) .

As an example of **Iontronics** we present the morphological control of fractal PPy. For instance, if the electrolysis polymerization is performed under the condition of constant current, the generation amount of radical cations per unit time is constant. If the radical coupling reaction is assumed, the density of the activated species of reaction becomes constant without any relation to the concentration of monomer and growth patterns with two dimensional broad leaf are obtained. On the other hand, If the electrophilic substitution coupling reaction is assumed, the reactive probability of the radical cation and monomer increases as the concentration of monomer increases, and growth patterns like three dimensional needle leaf are obtained. FIGURE 4 shows examples of morphological control of conductive PPy by changing polymerization current.

4.6 Conductive polymers as bioelectronic materials

At present, though it is made with the metal electrode such as ITO (indium tin oxide) and platinum as a nerve stimulation electrode, the compatibility of the biological tissue and the metal electrode becomes a problem. As measures, up to date the surface of the electrode was covered by having used collergen that was one of the matrices outside the cell (existing supermolecular structure besides the cell inorganism) and poly(lysine) that was the cell attachment factor (interceller bonding) and compatibility was given. However, it caused an increase in impedance by covering the surface of the electrode and decreased the efficiency of the input and output stimulus signals. Therefore, it is necessary to develop the nerve stimulation electrode which possesses compatibility with the biological tissue and the efficiency of the stimulus signal is not decreased, and it is extremely important in the progress of nerve interface technology.

On the other hand, conductive polymers with extensive π electron conjugative systems in their main chain are considered to be organic semiconductors with relatively small bandgaps, and their basic properties and functional applications, *etc.* are being intensively studied as new materials in the field of physical chemistry. If such conductive polymers have a high biocompatibility compared with the metal, the functional application in biomedical engineering as a new artificial internal organ material is expected.

To develop nerve stimulation electrodes of the inside of the body burial type, poly(3,4-ehtylenedioxythiophene) (PEDOT) and polypyrrole (PPy) of biocompatibility was mainly evaluated in the present study. For the biocompatibility of PEDOT and/or

PPy, the neuronal cell culture experiment was performed and evaluated. Fibroblastic cell L929 removed from the mouse on the fabricated PEDOT and/or PPy films were cultured, and their survival and growth were observed.

The fibroblastic cell is one of the cells that compose the mouse uniting organization, and its cytoplasm shows that nucleoli has clear oval nucleus and shows a base good nature.

FIGURE 5. shows the appearance of fibloblastic cell L929 culture, (a) on dish without collagen, (b) on PPy doped with TBABr and (c) on PEDOT doped with $TBABF_4$. From FIGURE 5 (a), the cell proliferates on the dish surface and to all aspects of the dish in 96h. On the other hand, from FIGURE 5 (b) and (c), fibroblastic L929 exhibited good adhesion on PPy doped with TBABr- and PEDOT doped with $TBABF_4$- coated ITO surfaces as well as the culture experiment that uses the dish. After 24 h, it is understood that the cell is bonded on conductive polymer films and proliferates. 96 h later, the cell proliferated to all aspects of the conductive polymer films, PPy and PEDOT, respectively. Though dopants that conductive polymer films possess differ from TBABr in the PPy film and $TBABF_4$ in the PEDOT film, it seems that the kind of dopants don't influence cell proliferation.

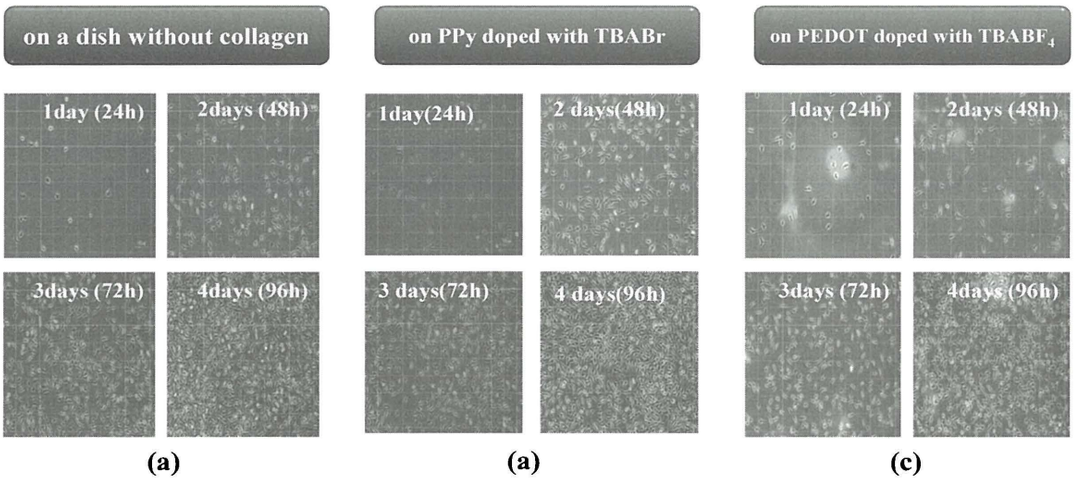


FIGURE 5. Appearance of fibroblastic cell L929 culture.

Fibroblast L929 and myoblast C2C12 cells of the mouse uniting organization origin were sown to the conductive polymer films (PPy and/or PEDOT), and the proliferative process of these cells was observed. The L929 fibroblast and C2C12 myoblast cells were observed to proliferate almost similarly with the cell cultured without changing the form on a dish on the market and to maintain compatibility. In addition, it was able to confirm that the C2C12 myoblast caused an induced differentiation on these conductive polymers films after the subconfluent and formed a myotube fibrous cell. In other words, two kinds of conductive polymers used in this study, PPy and PEDOT films maintained the secretion function of the cell cultured at those surface. Therefore, the PPy- and the PEDOT-coated electrode suggested the possibility of being used as a nerve stimulation electrode with biocompatibility because it was effective to culture the cell.

4.7 Electrochromism

As section 3, it is not clarified enough of various influences like the solvent, the supporting electrolyte, the polymerization voltage, and the polymerization temperature, *etc.* on the electrolysis polymerization reaction. Because various factors like the composition and the electrolytic condition of electrolyte *etc.* take part in the very complexity with the electrode reaction, the reaction mechanism of the conductive polymer synthesis by the electrolysis polymerization technique has not been clearly clarified under the present situation.

The electrochemical switching between the neutral and doped states of conductive polymers also causes the concurrence of a number of important changes. The bipolaron states in a doped polymer are located in the gap between the conduction and valence bands as shown in FIGURE 6. New electronic transitions are thus available to absorb photons often in the red to near infrared range. In the meantime, the band gap of the polymer is enlarged.

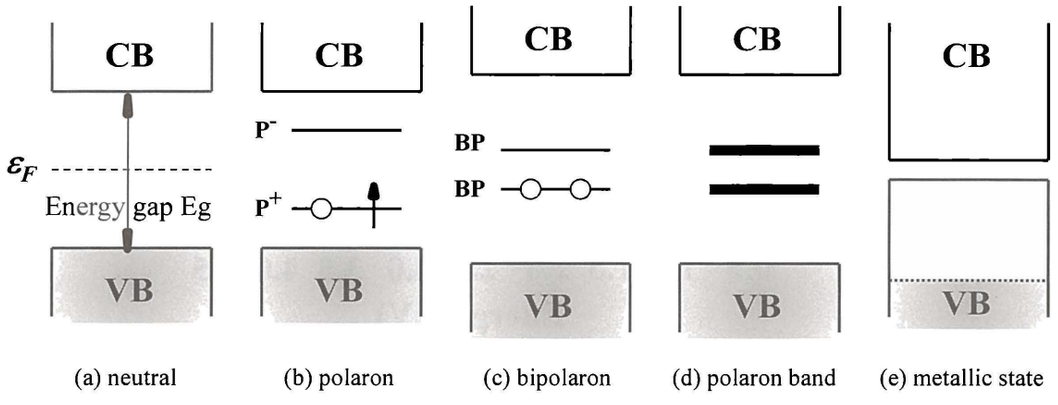


FIGURE 6. Band structure and electronic transitions in a conductive polymer.

Jonas and Schrader[11] found that poly(3,4-etrhylenedioxythiophene), PEDOT, with the molecular structure shown in FIGURE 7 is extremely transparent and its stability is excellent under a typical environment. When the conductive polymer is actually applied, the environmental stability becomes extremely important. It is considered that doped polypyrrole and polythiophene, have excellent stability compared with that of positively charged polyacetylene, because of the stabilization effect of the positive charge with the nitrogen atom and the sulfur atom. On the other hand, because of the β position in PEDOT is oxidized easily and blocked by

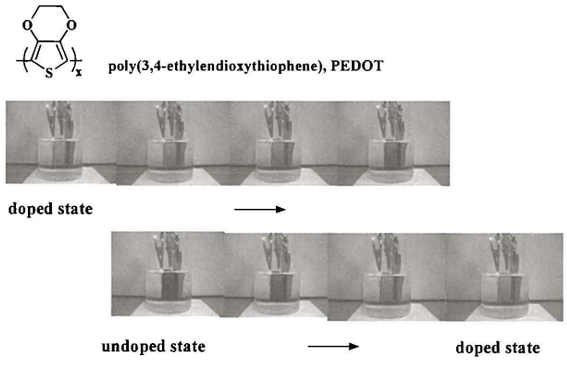


FIGURE 7. Color change of poly(3,4-ethylenedioxythiophene), PEDOT owing on redox reaction.

the ethylenedioxy groups, this material has high thermal stability and is excellent in high temperature and stable for a long time compared with PPy. In general, it is well known electrical, optical or electrochemical properties of conductive polymers changed suddenly owing to the reversible doping. FIGURE 7 shows the color change based on the redox reaction of PEDOT films. The PEDOT film is light blue or almost transparent in the doped state, and deep blue in the undoped state.[8] And then, the color change is reversible in the PEDOT films.

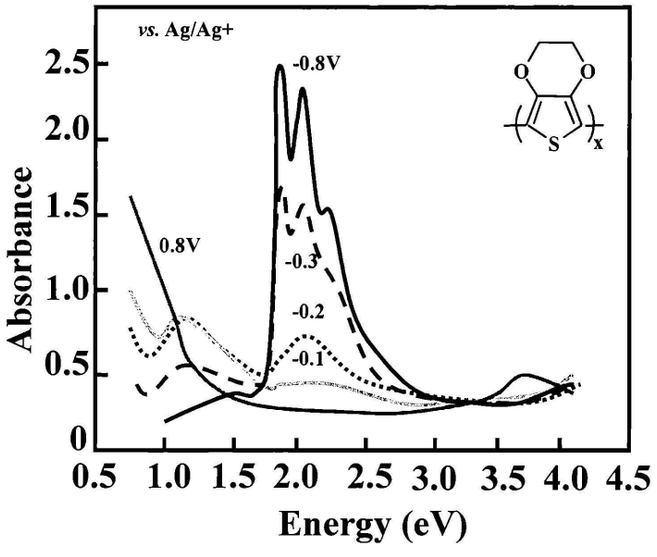


FIGURE 8. Optical absorption spectral change of PEDOT film taken during electrochemical doping.

On the other hand, FIGURE 8 shows the change in the optical absorption spectrum of the PEDOT film with the doping potential.[8] The films in the neutral and reduced states show strong absorption in the visible region and are deep blue in color. With increasing doping potential, the optical absorption in the visible region decreases and the film becomes light blue or transparent in the oxidized state from deep blue.

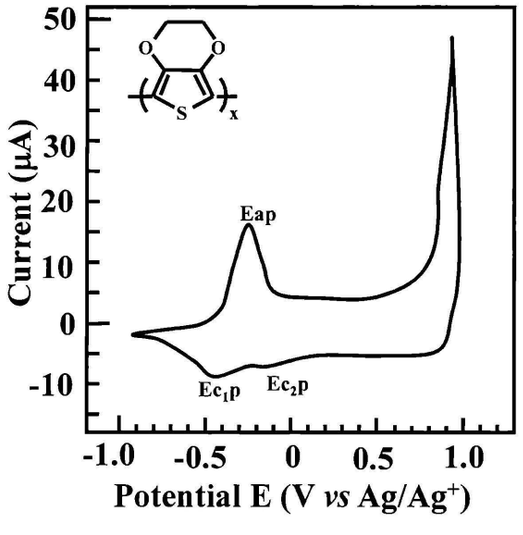


FIGURE 9. Cyclic voltammmogram of PEDOT film.

In contrast, clear peaks that show the electrochemical properties of the PEDOT film are observed in the oxidation and reduction curves as shown in FIGURE 9. That is, the peaks of the oxidation and reduction curves appear at around -0.3 V vs Ag/Ag^+ and about -0.5 and -0.2 V vs Ag/Ag^+, respectively, and reversible doping is possible.

5. Summary

In November, 1978, Luigi Garvani (9 September, 1937 ~ 4 December, 1798) had been examining on the dissection of the frog. When the scalpel made from two kinds of metal was exposed to the nerve of the frog, he had discovered that it moved as if the leg of the frog lived. This laboratory finding sawed the interest of many researchers and led to the development of electrochemistry.

He had clarified

"Electricity and muscle contraction are related."

The above mentioned development highlights the diversity and importance of Iontronic organic materials and devices. The field is intertwined with so many other fields that a complete review of its history and all the important discoveries is almost impossible. Here, I have provided merely my personal view on what occurred in the past that shaped the field as it is today. A more detailed investigation is necessary.

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